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STRIPPING OR TRANSFERRING PLATINUM METALS

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This invention relates to the dissolving of metals of the platinum group, and is particularly applicable to the removal of a coating of such metals from a metal foundation. At the present time, with the single exception of the removal of palladium from a silver foundation, there is no satisfactory method of removing deposits of the platinum metals from their foundations, so that if the plating on an article is defective the article may have to be scrapped. In other known processes for dissolving platinum metals such, for example, as those involving the use of fused bisulphates of the alkali metals to dissolve rhodium, the underlying foundation metals are preferentially attacked in the stripping bath with resultant serious local pitting which renders the articles useless for further coating processes.

According to the present invention, articles from which it is desired to remove a platinum metal coating are immersed in a molten bath comprising either potassium cyanide or sodium cyanide or a mixture of these. It is found that the platinum metal coating is attacked by the constituents of the bath and is progressively removed until the foundation metal begins to be exposed. When this happens, both the foundation metal and the platinum metal coating will in general be attacked, and the commercial utility of the present process depends on the discovery that in many cases the platinum metal coating is preferentially attacked, that is to say, there is no substantial corrosion of the foundation metal until the complete removal of the platinum metal. For a coating of any given platinum metal, the nature of the foundation metal which can be used in the present process depends on the relative degree of attack of the cyanide bath on the platinum metal coating and the foundation metal; it is necessary if the present process is to be applicable that the platinum metal should be preferentially attacked. Of course, the process cannot be applied to articles containing a foundation metal which would melt or be adversely affected at the temperature necessary to maintain the bath in a molten condition. The foundation metals to which coatings of the platinum metals are most frequently applied are nickel, copper, silver and gold. The range of applicability of the novel process to coatings on these metals is indicated in the following table in which the metals are arranged approximately in the order of the readiness with which they are attacked by the cyanide bath:

Rhodium,
Nickel,
Iridium,
Ruthenium,
Copper, gold, platinum,
Palladium,
Silver.

Thus, any of the platinum metals can be stripped from a silver foundation, but rhodium alone can be stripped from nickel.

It has been found that the solution of the platinum metals in the bath can be accelerated by the use of an electric current. According to a further feature of the invention, therefore, a molten cyanide bath is employed as the electrolyte in an electrolytic process for dissolving platinum metals from an anode, whether the platinum metals are in the form of a coating or not. It has been found that in such a process the anodic current efficiency is greater than the cathodic current efficiency, i. e. the amount of platinum metal going into solution at the anode is greater than that deposited at the cathode, and, accordingly, one result of the process is to build up a complex cyanogen compound of a platinum metal in the electrolyte. This process may, therefore, be used as a step in the preparation of cyanogen compounds of the platinum metals.

According to a further feature of the present invention, some article which it is desired to coat with a platinum metal or a platinum metal alloy may constitute the cathode of the electrolytic bath. The anode in this case consists either of an article coated with a platinum metal or the metal itself, or again there may be used a plurality of anodes coated with or consisting of different platinum metals so as to deposit an alloy at the cathode. In order to accelerate the deposition on the cathode it is desirable to add to the electrolytic bath a small quantity of the complex alkali metal cyanide of the platinum metal or metals under treatment, since otherwise deposition on the cathode will not begin until a certain quantity of this salt has been formed in the bath. The addition of such a complex platinum metal cyanide however is not essential, and in particular in the case of

rhodium it is possible to transfer rhodium from an anode to the cathode with the use of an electrolyte initially free from any rhodium cyanogen compounds.

The cyanide bath contains potassium cyanide or sodium cyanide or both these substances and since it is as a rule desirable to keep the temperature of the molten bath as low as possible in order to avoid damaging any soldered joints or softening work-hardened metal, it is generally advisable to add some inactive substance in order to lower the melting point of the bath. It is generally preferable to add caustic alkali for this purpose and the bath itself preferably comprises a mixture of potassium cyanide and sodium cyanide since such a mixture has a lower melting point than either of the two pure substances. A very convenient cyanide mixture in practice contains three parts of sodium cyanide and two of potassium cyanide. The addition of a sufficient quantity of caustic soda to such a mixture will bring the melting point as low as 300° C. The addition of caustic alkali, however, generally gives rise to frothing and gassing and consequently it should only be used when it is desirable that the temperature of the bath should be brought down below the melting point of the pure cyanide bath. In certain cases potassium or sodium ferrocyanide or ferricyanide may be added to the bath, but these may tend to make the rate of solution slower. Since there is some tendency for the molten cyanides to oxidize in the air the process may be carried on under non-oxidizing conditions, for example by using an inert atmosphere or by covering the molten cyanide bath with a protective layer such as a mixture containing graphite and plumbago.

The following examples illustrate the invention.

Example 1

In the removal of rhodium from silver, a mixture consisting of 3,500 grams "double cyanide" (75% NaCN, 25% KCN) and 466 grams of 95% potassium cyanide was fused in an iron basin at a temperature of about 500° C. Simple immersion of the coated article in this bath for about ten minutes followed by light buffing was sufficient completely to strip the rhodium deposit.

Example 2

In the removal of rhodium from copper, a mixture consisting of 20% potassium cyanide, 30% sodium cyanide and 50% caustic soda was fused in an iron crucible at a temperature of about 440° C. Simple immersion of a rhodium-plated copper article having a coating thickness of $50–60\times10^{-6}$ inch for fifteen minutes led to removal of 35% of the coating, but on constituting the article the anode of an electrolytic bath by suspending it from a graphite hook and passing a current of density 2 amps/dcm², the coating was entirely stripped in five minutes.

Example 3

As another example of the removal of rhodium from copper, a mixture consisting of 12% potassium cyanide, 18% sodium cyanide and 70% caustic soda was fused in an iron crucible at a temperature of about 305° C. Passage of a current of density about 2 amps/dcm² led to stripping of a rhodium coating of 60×10^{-6} inches thick in 10 minutes.

Example 4

A bath consisting of 60% sodium cyanide and 40% potassium cyanide in an iron bowl or porcelain crucible was found satisfactory for stripping palladium and platinum from a silver foundation, ruthenium from copper and iridium from gold either by simple immersion or by anodic treatment, the article to be stripped being in the latter case suspended either by a graphite hook or a silver wire. In the case of thick coatings of palladium and platinum (100×10^{-6} inches) on silver, anodic treatment is preferable because the rate of solution is much more rapid than with simple immersion.

Example 5

To deposit ruthenium onto a gold cathode, an electrolyte was used consisting of 7.5 parts sodium cyanide, 5 parts potassium cyanide and 2 parts potassium ruthenocyanide in a porcelain crucible in an atmosphere of nitrogen at a temperature of 520–550° C. A current of density about 2 amps/dcm² was passed using a ruthenium anode and gold cathode. About 0.64 part of the anode was dissolved in five hours, and of these 0.23 part was deposited on the cathode, the remainder of the ruthenium being left in the electrolyte in the form of a complex cyanide. This process was found suitable for providing gold pen nibs with ruthenium tips.

I claim:—

1. A process of stripping platinum metals from a metal foundation which comprises making an article having a platinum metal coating, which is to be stripped, the anode of an electrolytic bath comprising a molten alkali metal cyanide of the group consisting of sodium cyanide and potassium cyanide at a temperature above the melting point of said cyanide and below the melting point of said platinum metal, and passing electric current through said bath to effect the stripping of said platinum metal from said metal foundation without any substantial corrosion of the latter.

2. A process for the transference of one or more platinum metals from one or more articles having a foundation metal and a platinum metal coating to another article which comprises making an article having a platinum metal coating an anode in an electrolytic bath comprising a molten alkali cyanide of the group consisting of sodium cyanide and potassium cyanide at a temperature above the melting point of said cyanide and below the melting point of said platinum metal and the article on which a platinum metal is to be deposited the cathode, and passing electric current through said bath to effect a transference of a platinum metal from said anode to said cathode without any substantial corrosion of the foundation metal of the article constituting the anode.

3. A process of stripping platinum metals from a metal foundation which comprises immersing an article having a platinum metal coating, which is to be stripped, in a molten bath of a mixture of potassium cyanide, sodium cyanide and sodium hydroxide in the proportions by weight of about 12, 18 and 70, respectively, at a temperature above the melting point of said cyanides and below the melting point of said platinum metal to effect the stripping of said platinum metal from said metal foundation without any substantial corrosion of the latter.

4. A process of stripping platinum metals from a metal foundation which comprises making an article having a platinum metal coating, which

is to be stripped, the anode of an electrolytic bath comprising a mixture of molten potassium cyanide, sodium cyanide and sodium hydroxide in proportions by weight of about 12, 18 and 70, respectively, at a temperature above the melting point of said cyanides and below the melting point of said platinum metal, and passing electric current through said bath to effect the stripping of said platinum metal from said metal foundation without any substantial corrosion of the latter.

5. A process for the transference of one or more platinum metals from one or more articles to another article which comprises making an article having a platinum metal coating an anode in an electrolytic bath comprising a mixture of molten potassium cyanide, sodium cyanide and sodium hydroxide in proportions by weight of about 12, 18 and 70, respectively, at a temperature above the melting point of said cyanides and below the melting point of said platinum metal and the artitcle on which a platinum metal is to be deposited the cathode, and passing electric current through said bath to effect a transference of a platinum metal from said anode to said cathode without any substantial corrosion of the foundation metal of the article constituting the anode.

6. A process of stripping platinum metals from a metal foundation which comprises immersing an article having a platinum metal coating, which is to be stripped, in a molten bath of an alkali metal cyanide maintained under non-oxidizing conditions and at a temperature above the melting point of said cyanide and below the melting point of said platinum metal to effect the stripping of said platinum metal from said metal foundation without any substantial corrosion of the latter.

7. A process of stripping platinum metals from a metal foundation which comprises immersing an article having a platinum metal coating, which is to be stripped, in a molten bath of an alkali metal cyanide at a temperature above the melting point of said cyanide and below the melting point of said platinum metal to effect the stripping of said platinum metal from said metal foundation without any substantial corrosion of the latter, said bath containing at least one inactive substance capable of lowering the melting point thereof which substance is a member of the group consisting of sodium hydroxide and potassium hydroxide.

8. The process set forth in claim 1 in which the bath is maintained under non-oxidizing conditions.

9. The process set forth in claim 1 in which the bath contains at least one inactive substance capable of lowering the melting point thereof of the group consisting of sodium hydroxide and potassium hydroxide.

10. The process set forth in claim 2 in which the bath is maintained under non-oxodizing conditions.

11. The process set forth in claim 2 in which the bath contains at least one inactive substance capable of lowering the melting point thereof of the group consisting of sodium hydroxide and potassium hydroxide.

12. The process set forth in claim 2 in which the bath contains a complex alkali metal cyanide of the platinum metal which is to be transferred.

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